Functional Properties of a Food Colorant
Prepared from Red Cabbage

G. M. SAPERS, I. TAFFER, and L. R. ROSS

──────────── ABSTRACT ────────────

Spectral, colorant, and stability properties of colorants based on red cabbage, grape, cranberry, beet, and Red No. 40 were compared in buffer and in a simulated beverage. At pH 3, red cabbage imparted a red color similar to that of beet juice and less orange than that of the other colorants. Increasing the pH of red cabbage extracts to 4 produced a bathochromic shift and decreased color strength. Tristimulus parameters displayed maxima when L was varied. Red cabbage pigments were more stable during heating and storage than were the other colorants tested. pH had little effect on color stability; exposure to light greatly increased color loss during storage.

INTRODUCTION

CONSIDERABLE INTEREST has been shown in the utilization of unconventional colorants as replacements for synthetic red food dyes since the banning of FD&C Red Nos. 2 and 4 and the threatened loss of Red No. 40. Natural colorants have not yet proven satisfactory as substitutes for the synthetic dyes because of their high cost, limited supply, and technical limitations (Riboh, 1977).

Shewfelt and Ahmed (1977, 1978) proposed that red cabbage (*Brassica oleracea*) be used as a colorant for dry soft drink mixes. They demonstrated that pigment preparations obtained from this plant imparted a color superior to that obtained with Red No. 40. Color stability was satisfactory both in the dry state and in reconstituted beverage mixes during refrigerated storage. Preliminary studies conducted in our laboratory with carbonated beverages containing red cabbage pigments also suggested a high degree of color stability.

The pigments of red cabbage consist primarily of cyanidin 3-sophoroside-5-glucoside and cyanidin 3-sophoroside-5-glucoside acylated with sinapic, ferulic, p-coumaric, and malonic acids (Tanchev and Timberlake, 1969; Hrazdina et al., 1977). Van Buren et al., (1968) reported that acylated anthocyanins were more stable to light than were nonacylated anthocyanins.

The objectives of our research were twofold: (1) to characterize the spectral and colorant properties of red cabbage pigments at pH values between 3 and 4 and compare them to other natural colorants; and (2) to determine the stability of red cabbage pigments in aqueous solution as a function of pH, light, and temperature.

EXPERIMENTAL

Colorant preparation

Fresh red cabbage samples representing ten different cultivars (Debut, Hybrid Red YR150, Red Storage 4004, Mammoth Red Rock, Meteor, Red Danish, Red Drumhead, Red Head Hybrid, Resistant Red Acre, and Ruby Ball) were obtained from Fordhook Farms, the experiment station of the W. Atlee Burpee Co. in Doyles-

town, Pa. Cabbages were quartered, cored, and blended with 1% HCl in MeOH (1:1 w/v) in a 1 gal Waring Blendor. The resulting homogenates were held overnight at room temperature and then filtered, first through cheesecloth and then through Whatman No. 1 filter paper in a centrifugal filtration device. Filtrates were refrigerated and then further clarified by the addition of 1% Celite Analytical Filter-Aid (Johns-Manville Products Corp., Lompoc, Cal.) followed by filtration through Whatman No. 2 paper with suction. The clarified filtrates were concentrated ten to twentyfold with a Thomas Magne-Flash Evaporator Model 38 (Arthur H. Thomas Co., Philadelphia, Pa.) operated at a water bath temperature of 35-40°C and a vacuum of 0.03 kg/cm² (29 in Hg). Foaming was controlled by the application of Dow Corning Antifoam A Spray (Dow Corning Corp., Midland, Mich.) Pigment concentrates were frozen and stored at −18°C until required.

Samples of other natural and synthetic colorants were obtained from commercial sources so that their functional properties could be compared with those of red cabbage pigments. These samples included a grape concentrate, cranberry concentrate, beet juice concentrate, and FD&C Red No. 40.

Measurement of spectral and colorant properties

Aqueous pigment solutions were prepared by diluting concentrates with pH 3, 3.5 or 4 McIlvaine's buffer (Hodgman, 1954) and then readjusting to the original pH value of the buffer by adding 10% NaOH to compensate for the high acidity of the pigment preparations. The pigment solutions were diluted further with buffer so that absorbance and tristimulus coordinate measurements would fall within a useful range. Additional dilutions were made at pH 1 and 4.5, following the procedure of Fuleki and Francis (1968), so that values of their Simplified Degradation Index could be calculated for the anthocyanin-based colorants. A Perkin-Elmer Model 552 UV-VIS Double Beam Spectrophotometer (Perkin-Elmer Corp., Norwalk, Conn.) was used to measure λ_{max} and corresponding absorbance values for visible absorption bands. A Gardner XL-23 Tristimulus Colorimeter (Gardner Laboratory, Inc., Bethesda, Md.), operated in the transmission mode, was used to obtain values of the tristimulus coordinates L, a_L, and b_L for a series of colorant dilutions ranging in absorbance at λ_{max} between 0.4 and 3.0. Tristimulus measurements were made in a clear glass optical cell, 57.1 mm in diameter (ID) and 40 mm in height, filled to a depth of 20 mm with a 50-ml sample.

To determine the pH sensitivity of anthocyanin-based colorants, absorbance values for pH 3, 3.5, and 4 solutions were expressed as a percentage of the absorbance obtained at pH 1. To compare the color strength of different colorants, the quantity of product (or raw material, in the case of red cabbage) required to produce an absorbance at λ_{max} of 1.0 in 1L of pH 3.0 buffer was estimated from the spectral data and appropriate dilution factors. Values of the hue angle θ ($\tan^{-1} b_L/a_L$) and saturation index $(a_L{}^2 + b_L{}^2)^{1/2}$ were computed from the tristimulus coordinates. Tristimulus parameters of colorants samples were compared at different degrees of lightness, including L-values corresponding to $A\lambda_{max} = 1.0$ and L = 50. In addition, since the tristimulus parameters are known to vary with L and may, in some cases, display a maximum (VanBuren et al., 1974), values of the hue angle were plotted against L for each colorant sample so that L-values corresponding to maxima could be determined.

Evaluation of heat stability

The heat stability of red cabbage pigments and other natural colorants was determined by immersing duplicate loosely capped 125 × 16 mm screw cap test tubes containing 12-14 ml of colorant solution in a boiling water bath for as long as 5 hr (depending on pigment losses) followed by cooling in an ice bath for 3 min. Color-

ant solutions to be heated were prepared with pH 3 or 3.5 McIl-vaine's buffer, adjusted in concentration so that the initial absorbance at λ_{max} was between 1.0 and 1.5. In addition, a solution of red cabbage colorant (Meteor cultivar) was prepared by diluting the pigment concentrate with a simulated beverage containing 10% sucrose and 0.3% citric acid monohydrate, adjusted to pH 3 ot 3.5 by titration with 10% NaOH solution. Following heating and cooling, the sample absorbance was measured at λ_{max} with a Bausch and Lomb Spectronic 88 Spectrophotometer.

Evaluation of storage stability

The storage stability of colorants prepared from red cabbage and cranberry concentrates was determined in air at 25°C by a procedure used previously for beet pigments (Sapers and Hornstein, 1979). Colorant concentrates were boiled 2 min to inactivate enzymes, cooled, clarified by the addition of 1% Celite followed by filtration through Whatman No. 2 paper with suction, diluted with pH 3 or 3.5 McIlvaine's buffer to a concentration yielding an absorbance at λ_{max} of 1.2-1.5, readjusted to the original pH of the buffer with 10% NaOH, sterilized by membrane filtration and dispensed aseptically into sterile tubes for storage. Stability tests were also conducted with the simulated beverage described previously instead of buffer; samples were adjusted to pH 3 and 3.5. Sample tubes were stored under fluorescent light (90-100 ft.-c) or in darkness for as long as 9 months.

Following storage, measurements of absorbance at λ_{max} and the tristimulus coordinates L, a_L, and b_L were made, as described previously.

Table 1—Spectral properties of colorants prepared from red cabbage extracts, grape concentrate, and cranberry concentrate

Colorant	pH	λ_{max}	% of absorbance at pH 1.0	Degradation index[b]
Red cabbage	3.0	524	43.1	1.17
extract[a]	3.5	528	29.6	—
	4.0	531	19.0	—
Grape	3.0	518	51.5	1.16
concentrate	3.5	519	32.0	—
	4.0	520	18.9	—
Cranberry	3.0	523	78.5	1.70
concentrate	3.5	526	64.5	—
	4.0	530	52.4	—

[a] Meteor cultivar
[b] Simplified Degradation Index, as defined by Fuleki and Francis (1968).

RESULTS & DISCUSSION

Spectral properties

To be suitable as replacements for synthetic food dyes, natural pigments should be capable of imparting the desired color over a useful pH range. The spectral and colorant properties of extracts of nine red cabbage cultivars, other natural colorants, and Red No. 40 were compared at pH values between 3 and 4, a pH range which encompasses many artificially colored food and beverage products. Visible absorption maxima (λ_{max}) for aqueous anthocyanin solutions vary with pH. All red cabbage cultivars studied were similar with respect to pH response and the general appearance of spectra. Data for Meteor cabbage, a more highly pigmented but otherwise similar cultivar, are given in Table 1. At pH 3, λ_{max} values for solutions of red cabbage pigments were between 519 and 526 nm, depending on the cultivar. Absorption maxima shited to 524-529 nm at pH 3.5 and to 526-534 nm at pH 4. Values of λ_{max} were higher for red cabbage than for grape at the same pH or for Red No. 40 (496 nm), which is not pH-sensitive. Absorption maxima were similar for red cabbage and cranberry colorants at the same pH. Values of λ_{max} for red cabbage solutions at pH 3-4 were lower than λ_{max} for beet juice concentrate (532 nm), which is not pH-dependent.

Increasing the pH of solutions containing red cabbage pigments not only produced a bathochromic shift but also substantially lowered their color strength, as measured by the absorbance at λ_{max}. Similar changes occurred with solutions of grape concentrate. The smaller pH effect seen with cranberry probably reflects the substantial contribution of degradation products to the sample absorbance at λ_{max}. This is consistent with the higher Degradation Index obtained with cranberry concentrate in comparison to that for red cabbage and grape. The pH sensitivity of these colorants within a relatively narrow pH range represents a serious limitation to their utilization.

Colorants prepared from the different red cabbage cultivars varied in color strength over a twofold range. These differences may be related to cultivar, maturity, extraction efficiency, or other factors. We have estimated from the spectral data that the quantity of colorant obtained from 26-63g of red cabbage, depending on the sample, would produce an absorbance at λ_{max} of 1.0 in 1L of pH 3 buffer solution; this absorbance also could be obtained with 23 mg of Red No. 40, 3 ml of beet juice concentrate, 6 ml of

Table 2—Colorant properties of red cabbage extracts and other colorants

		Tristimulus value								
		Constant absorbance ($A\lambda_{max}$ = 1.0)					Constant L value (L = 50)			
Colorant	pH	L	a_L	b_L	θ	Sat'n index	a_L	b_L	θ	Sat'n index
Cabbage	3.0	50.5	75.4	6.4	4.9	75.7	78.3	8.9	6.5	78.9
ext.[a]	3.5	45.2	75.4	3.8	2.9	75.6	74.5	1.3	1.0	74.5
	4.0	39.7	72.6	−2.6	357.9	72.6	65.0	−7.5	353.4	65.5
Grape	3.0	49.0	67.4	20.4	16.8	70.4	66.6	19.8	16.5	69.5
conc[b]	3.5	42.8	65.7	19.0	16.1	68.4	61.0	16.3	15.0	63.2
	4.0	35.3	61.2	16.0	14.7	63.3	51.8	13.2	14.3	53.5
Cranberry	3.0	39.7	66.9	19.1	15.9	69.5	59.1	16.8	15.8	61.4
conc[b]	3.5	35.3	64.0	17.0	14.9	66.3	52.9	14.7	15.5	54.9
	4.0	32.2	61.8	15.1	13.7	63.7	47.8	12.8	15.0	49.5
Beet	3.0	42.7	80.3	9.5	6.8	80.7	73.9	1.2	0.9	74.0
conc[b]	5.0	43.3	80.5	14.0	9.9	81.7	74.0	7.5	5.8	74.4
Red No. 40[b]	3.0	61.4	65.4	29.5	24.1	71.7	77.8	33.1	23.0	84.6
	4.0	61.4	65.4	29.5	24.1	71.7	77.4	33.1	23.2	84.2

[a] Meteor variety
[b] Commercial colorant

grape concentrate, or 35 ml of cranberry concentrate. The pigment contents of these products were not estimated since data on the proportions of individual anthocyanins and their extinction coefficients were not available for the red cabbage extracts. The relatively low color strength obtained with cranberry concentrate may be a consequence of pigment loss during processing or storage, as indicated by the higher Degradation Index of this colorant.

Colorant properties

Comparisons of the colorant properties of red cabbage pigments, other natural colorants, and Red No. 40 were based on tristimulus measurements made on solutions at pH 3-4, diluted to provide a wide range of color strengths (Table 2). Values of the tristimulus coordinates L, a_L, and b_L, as well as the hue angle θ and saturation index were similar for red cabbage colorants prepared from seven different cultivars at each of the pH's tested. Increasing the pH of cabbage pigment solutions, adjusted in concentration to $A\lambda_{max} = 1.0$, tended to make them darker (lower L) and more blue (lower b_L). Solutions adjusted in concentration to constant lightness (L = 50) became less red (lower a_L) with increasing pH. In both cases, the change in hue angle θ with increasing pH was indicative of a color change from orange-red at the lower pH to violet-red at the higher pH.

Solutions of red cabbage pigments and other colorants differed in lightness when compared at $A\lambda_{max} = 1.0$ (Table 2). Red cabbage produced darker solutions (lower L) than did Red No. 40, but was similar in lightness to grape and was lighter (higher L) than were solutions of cranberry and beet concentrates. Red cabbage pigments produced a less orange shade of red (lower hue angle θ) than did the other colorants, except for beet pigment which was similar. This is a reflection of slightly higher a_L values and much lower b_L values for red cabbage and beet pigments. The saturation index, an indication of color purity, generally paralleled a_L.

pH-Related color differences appeared to be greater with red cabbage pigments than with the other colorants in this study. This is evident in the spread of b_L and θ values at pH 3-4. The color and tristimulus coordinates of Red No. 40 solutions were not affected by pH; a small increase in b and hue angle occurred when the pH of beet juice was increased from 3 to 5.

With each of the colorants compared in this study, the chromaticity parameters (a, b, θ, and the saturation index) generally increased to a maximum value and then decreased as the pigment concentration was increased. L-values corresponding to these maxima (L_m) are given in Table 3. Differences in L_m between red cabbage cultivars were small. Maximum values of a and the saturation index occurred at similar L-values with red cabbage, grape, and beet colorants; with cranberry, these maxima appeared at lower L-values. Maxima for b and θ occurred at lower L-values with red cabbage extracts than with the other colorants. Chromaticity parameter maxima were not observed with cranberry concentrate (θ at pH 3.5 and 4), beet juice concentrate (b and θ), and Red No. 40 (a and the saturation index). With the anthocyanin-based colorants, increasing the pH shifted the maxima to lower L-values.

Van Buren et al. (1974) suggested that an anthocyanin solution observed in a container such as a wine glass, for which the light path varies over a wide range, would exhibit a variety of hues according to the θ vs L relationship. However, Eagerman et al. (1973) reported that the appearance of such solutions did not agree with the predicted hue at lower L-values; i.e., on dilution, colorant solutions might shift in hue with increasing L but would not return towards the original hue of the concentrated solution when L_m was

exceeded. They attributed the discrepancy to an inherent weakness in the equations relating chromaticity parameters to the X, Y, Z color scale. This error could affect the accuracy of color measurements made on dark-colored, highly concentrated pigment solutions. In our study, however, all tristimulus data for red cabbage extracts and beet juice concentrates reported herein corresponded to L-values greater than L_m. Values of b and θ for pH 4 grape concentrate and for cranberry concentrate at $A\lambda_{max} = 1.0$ (Table 2) did correspond to L-values near the maximum and consequently would be subject to error. Johnson et al. (1976) obtained relatively poor correlations between Gardner b or hue values and visual rankings or the anthocyanin concentration of cranberry juice cocktail samples, although they stated that their samples were not dark enough to be sub-

Table 3—Chromaticity parameter maxima with red cabbage extracts and other colorants

Colorant	pH	L-value at maximum			
		a	b	θ	Sat'n index
Cabbage ext.[a]	3.0	41-44	34-38	33-37	39-41
	3.5	38-41	28-33	27-32	37-39
	4.0	32-33	22-26	20-25	30-33
Grape conc[b]	3.0	39	41	41	39
	3.5	36	37	39	36
	4.0	32	35	38	32
Cranberry conc[b]	3.0	35	38	43	35
	3.5	29	35	>58[c]	31
	4.0	27	33	>56[c]	28
Beet conc[b]	3.0	39	<32[c]	<32[c]	37
	5.0	39	<34[c]	<34[c]	37
Red No. 40[b]	3.0	<49[c]	53	57	<49[c]
	4.0	<49[c]	53	58	<49[c]

[a] Range for 7 cultivars
[b] Commercial colorant
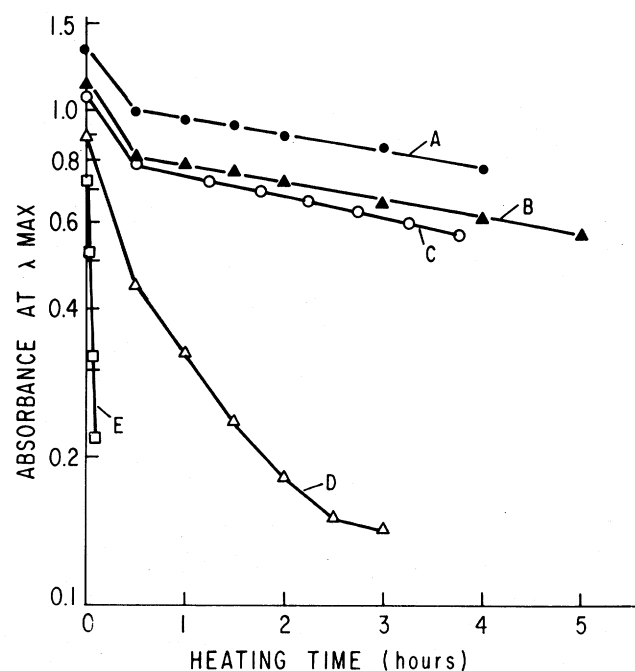[c] No maximum observed with dilutions tested

Fig. 1—Effects of heating at 100°C on the absorbance of pH 3 buffer solutions of colorants: (A) Meteor cabbage; (B) Resistant Red Acre cabbage; (C) Red Head cabbage; (D) cranberry concentrate; and (E) red beet.

ject to the L_m error.

Heat stability of red cabbage pigments

Measurements of the change in absorbance at λ_{max} of colorants prepared from three red cabbage cultivars (Red Head, Resistant Red Acre, and Meteor), cranberry concentrate, and red beet (Detroit Dark Red cultivar; data taken from Sapers and Hornstein, 1979), diluted with pH 3 buffer and heated at 100°C, are compared in Figure 1. Semi-log plots of the red cabbage stability data show an initial decrease in absorbance during the first 30 min of heating, followed by a more gradual decrease which appears to be linear. Pigment extracts obtained from the three red cabbage cultivars yielded similar stability curves and displayed a much greater degree of heat stability than did the pH 3 solutions of cranberry concentrate or red beet juice. Differences in stability between anthocyanin-based colorants may be related to their degree of acylation, the acylated red

cabbage anthocyanins (Hrazdina et al., 1977) being more heat stable than the nonacylated cranberry anthocyanins (Zapsalis and Francis, 1965). Van Buren et al. (1968) reported that wines containing acylated pigments retained their color more completely during heating (6 days at 50°C) than did wines containing nonacylated anthocyanins.

The heat stability of a colorant prepared from Meteor cabbage was determined at pH 3 and 3.5 buffer and in a simulated beverage containing sucrose and citric acid at concentrations similar to those used in such products as carbonated beverages, fruit drinks, and frozen fruit pops. Semi-log plots of the absorbance vs heating time data gave similar curves with buffer and the simulated beverage at both pH values (Fig. 2). Other workers have reported that the heat stability of anthocyanins is independent of pH in the absence of air and is greater at lower pH values in the presence of air (Markakis, 1974). We suggest that our system approached the former condition as a consequence of the venting of dissolved O_2 and headspace air from the loosely capped sample tubes during the first few minutes of heating.
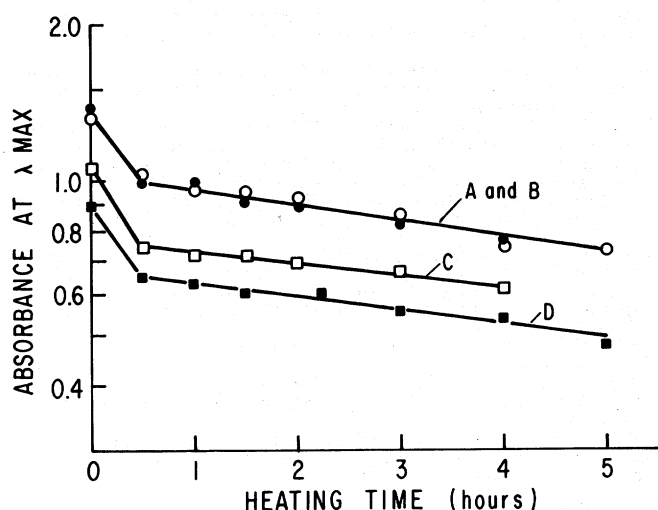

Fig. 2—Effects of heating at 100°C on the absorbance of solutions of Meteor cabbage colorant: (A) in pH 3 buffer; (B) in pH 3 simulated beverage; (C) in pH 3.5 simulated beverage; and (D) in pH 3.5 buffer.

Fig. 4—Effects of storage at 25°C on the absorbance of colorant solutions prepared from Resistant Red Acre cabbage: (A) pH 3 simulated beverage, darkness; (B) pH 3.5 buffer, darkness; (C) pH 3 buffer, darkness; (D) pH 3 simulated beverage, light; (E) pH 3.5 buffer, light; (F) pH 3 buffer, light.
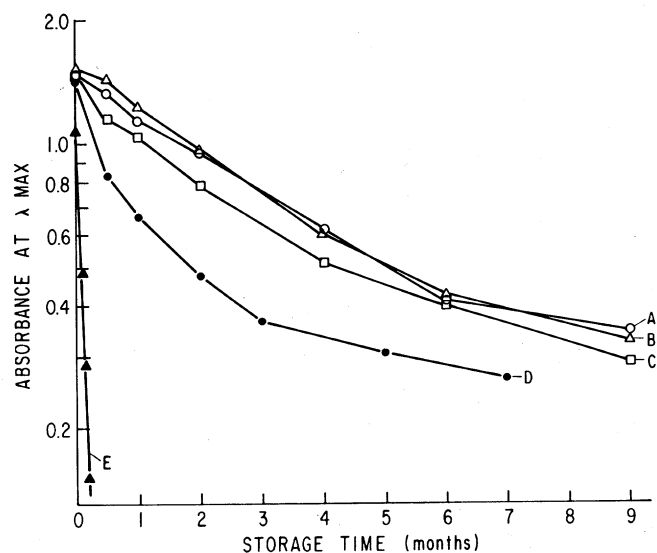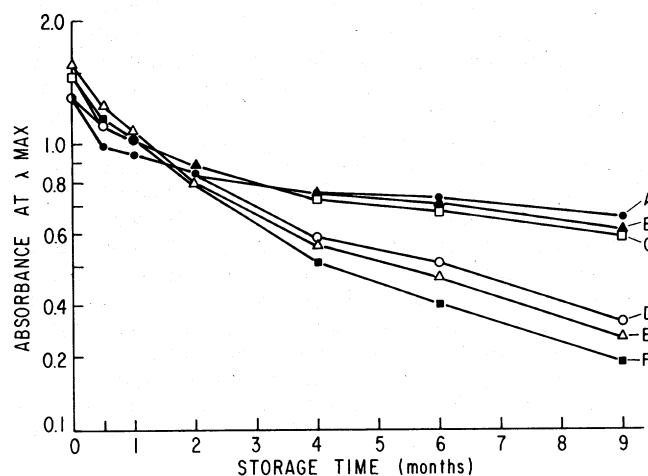

Fig. 3—Effects of storage in light at 25°C on the absorbance of pH 3 buffer solutions of colorants: (A) Meteor cabbage; (B) Red Head cabbage; (C) Resistant Red Acre cabbage; (D) cranberry concentrate; and (E) red beet.
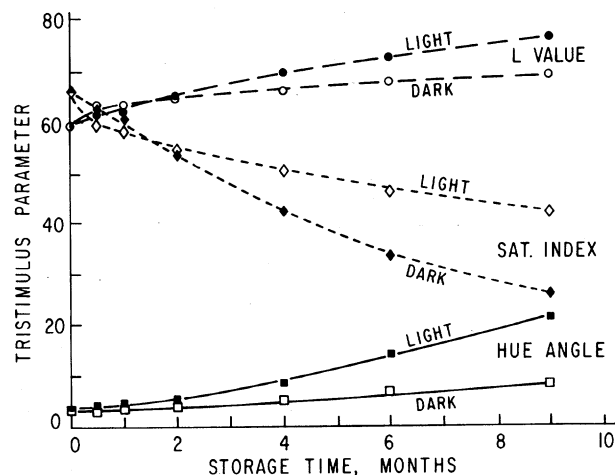

Fig. 5—Effects of storage at 25°C in light and in darkness on tristimulus parameters of Resistant Red Acre cabbage colorant in simulated beverage at pH 3.

Storage stability of red cabbage pigments

During storage at 25°C in air, the color of aqueous solutions of red cabbage pigments gradually faded and became more orange. Changes in the absorbance at λ_{max} of pH 3 solutions of colorants prepared from red cabbage (Resistant Red Acre, Red Head, and Meteor cultivars), cranberry concentrate, and red beet (Detroit Dark Red cultivar; data taken from Sapers and Hornstein, 1979) during storage in light at 25°C are shown in Fig. 3. The three red cabbage colorants responded similarly during storage, undergoing a progressive decrease in $A\lambda_{max}$. Solutions containing red cabbage colorant were more stable during storage than were solutions containing cranberry colorant. This may be due to the presence of acylated anthocyanins in the former, as discussed previously. Both red cabbage and cranberry colorants were much more stable during storage than was the colorant prepared from beef juice which had been evaluated under similar conditions in a previous study.

A smaller decrease in $A\lambda_{max}$ occurred when solutions of red cabbage colorant (Resistant Red Acre cultivar) were stored in darkness rather than in light (Fig. 4). This effect overshadowed relatively small differences between samples representing the two pH values and the simulated beverage formulation. Absorbance changes were consistently smaller in the simulated beverage than in buffer at both pH values and with all cultivars, in samples stored in the dark as well as in light. The basis of this protective effect is not known.

Visual changes in solutions of red cabbage colorant during storage can be represented by the L value, hue angle and saturation index, determined by tristimulus colorimetry (Fig. 1). Increasing L values indicate the extent of color fading during storage; changes were relatively small in samples stored in the dark. Increasing values of the hue angle in samples exposed to light indicate a shift in color from a red to a more orange-red shade. This may be due to the occurrence of browning reactions in parallel with anthocyanin degradation during storage. The decrease in saturation index, an indication of color purity or vividness (Van Buren et al., 1974), reflects the loss in redness due to anthocyanin degradation. Similar changes occurred at each of the pH values studied and in buffer as well as in the simulated beverage. These results demonstrate the high degree of color stability that can be attained with red cabbage colorant when light is excluded.

REFERENCES

Eagerman, B.A., Clydesdale, F.M., and Francis, F.J. 1973. Comparison of color scales for darker colored beverages. J. Food Sci. 38: 1051.

Fuleki, T. and Francis, F.J. 1968. Quantitative methods for anthocyanins. 2. Determination of total anthocyanin and degradation index for cranberry juice. J. Food Sci. 33: 78.

Hodgman, C.D. 1954. "Handbook of Chemistry and Physics," 36th ed., p. 1617. Chemical Rubber Publishing Co., Cleveland, Oh.

Hrazdina, G., Iredale, H., and Mattick, L.R. 1977. Anthocyanin composition of Brassica oleracea cv. Red Danish. Phytochemistry 16: 297.

Johnson, L.E., Clydesdale, F.M., and Francis, F.J. 1976. Use of expanded color scales to predict chemical and visual changes in solutions. J. Food Sci. 41: 74.

Markakis, P. 1974. Anthocyanins and their stability in foods. CRC Critical Reviews in Food Technol. March, p. 437.

Riboh, M. 1977. Natural colors: What works . . . what doesn't. Food Engr. May: 66.

Sapers, G.M. and Hornstein, J.S. 1979. Varietal differences in colorant properties and stability of red beet pigments. J. Food Sci. 44: 1245.

Shewfelt, R.L. and Ahmed, E.M. 1977. Anthocyanin extracted from red cabbage shows promise as coloring for dry beverage mixes. Food Product Development 11(4): 55.

Shewfelt, R.L. and Ahmed, E.M. 1978. Enhancement of powdered soft drink mixes with anthocyanin extracts. J. Food Sci. 43: 435.

Tanchev, S.S. and Timberlake, C.F. 1969. The anthocyanins of red cabbage (Brassica oleracea). Phytochemistry 8: 1825.

Van Buren, J.P., Bertino, J.J., and Robinson, W.B. 1968. Stability of wine anthocyanins on exposure to heat and light. Amer. J. Enology & Viticulture 19(3): 147.

Van Buren, J.P., Hrazdina, G. and Robinson, W.B. 1974. Color of anthocyanin solutions expressed in lightness and chromaticity terms. Effect of pH and type of anthocyanin. J. Food Sci. 39: 325.

Zapsalis, C. and Francis, F.J. 1965. Cranberry anthocyanins. J. Food Sci. 30: 396.

Ms received 2/15/80; revised 8/16/80; accepted 8/24/80.